

# Synthesis and Characterization of Novel Polyphenol Species Derived from Bis(4-aminophenyl)Ether: Substituent Effects on Thermal Behavior, Electrical Conductivity, Solubility, and Optical Band Gap

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**ABSTRACT:** In this study, four different Schiff bases namely 4,4'-oxybis[N-(2-hydroxybenzilidene)aniline] (2-HBA), 4,4'-oxybis[N-(4-hydroxybenzilidene)aniline] (4-HBA), 4,4'-oxybis[N-(3,4-dihydroxybenzilidene)aniline] (3,4-HBA), and 4,4'-oxybis[N-(4-hydroxy-3-methoxybenzilidene)aniline] (HMBA) were synthesized. These Schiff bases were converted to their polymers that have generate names of poly-4,4'-oxybis[N-(2-hydroxybenzilidene)aniline] (P-2-HBA), poly-4,4'-oxybis[N-(4-hydroxybenzilidene)aniline] (P-4-HBA), poly-4,4'-oxybis[N-(3,4-dihydroxybenzilidene)aniline] (P-3,4-HBA), and poly-4,4'-oxybis[N-(4-hydroxy-3-methoxybenzilidene)aniline] (PHMBA) via oxidative polycondensation reaction by using NaOCl as the oxidant. Four different metal complexes were also synthesized from 2-HBA and P-2-HBA. The structures of the compounds were confirmed by FTIR, UV-vis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses. According to  $^1\text{H}$  NMR spectra, the polymerization of the 2-HBA and 4-HBA largely maintained

with C—O—C coupling, whereas the polymerization of the 3,4-HBA and HMBA largely maintained with C—C coupling. The characterization was made by TG-DTA, size exclusion chromatography and solubility tests. Also, electrical conductivity of the polymers and the metal complex compounds were measured, showing that the synthesized polymers are semiconductors and their conductivities can be increased highly via doping with iodine ions (except PHMBA). According to UV-vis measurements, the optical band gaps ( $E_g$ ) were found to be 3.15, 2.06, 3.23, 3.02, 2.61, 2.47, 2.64, 2.42, 2.83, 2.77, 2.78, and 2.78 for 2-HBA, P-2-HBA, 4-HBA, P-4-HBA, 3,4-HBA, P-3,4-HBA, HMBA, PHMBA, 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 539–549, 2008

**Key words:** oxidative polycondensation; polyazomethine ether; thermal analysis; conductivity; optical band gap

## INTRODUCTION

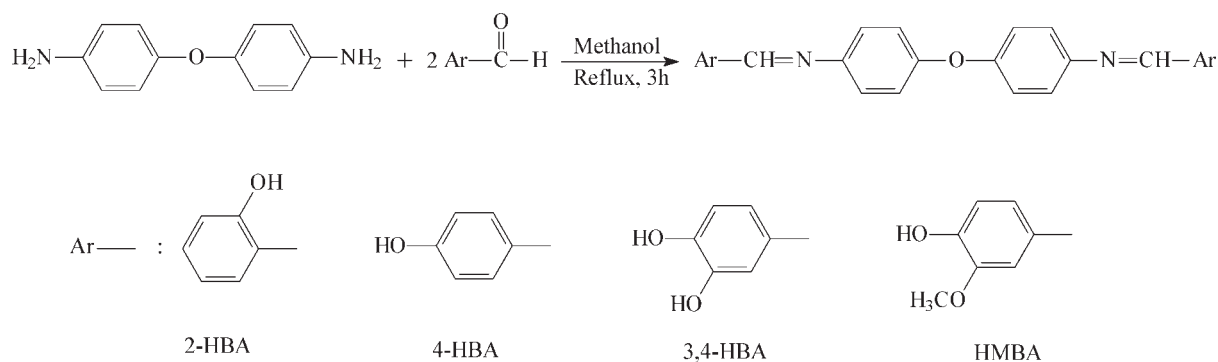
Polyazomethines (PAMs) and their derivatives have attracted much attention because of their useful properties such as high thermal stability, excellent mechanical strength, and good optoelectronic properties.<sup>1–4</sup> However, many synthesized PAMs, especially aromatic derivatives have low solubility in many organic solvents. With the aim of obtaining soluble PAMs many kinds of them have been previously prepared such as poly(azomethine ether)s,<sup>5</sup> poly(acrylate-azomethine)s,<sup>6</sup> poly(azomethine carbonate)s,<sup>7</sup> poly(amide-azomethine-ester)s,<sup>8</sup> poly(azomethine sulfone)s,<sup>9</sup> etc. Additionally, PAMs containing methoxy substituent have been presented with good solubility and also high thermal stability.<sup>10</sup> Oligo-

phenols and their —CH=N— containing derivatives have been synthesized by oxidative polycondensation method and presented in the literature with their several useful properties.<sup>11–15</sup> Using of water medium makes this method environmental harmless. Also, using of cheap oxidants such as NaOCl,  $\text{H}_2\text{O}_2$ , and air  $\text{O}_2$  is another advantage of this method. Additionally, because the synthesized products have good properties such as paramagnetism, semiconductivity, electrochemical cell, and resistance to high energy, this class of PAMs has become more attractive for researchers. During the last decade, Kaya and coworkers have studied this class of PAMs with thermal, electrochemical, optical, and electrical properties.<sup>16–18</sup> The synthesized products were also investigated as an antimicrobial agent.<sup>19</sup> It is seen that the synthesized PAMs have semiconductivity due to their polyconjugated bond systems.<sup>20,21</sup> Also, they have high thermal stability because of their highly aromatic structures.

For these reasons, we aimed to synthesize new soluble, semiconductive poly(azomethine ether)s via

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**Scheme 1** Synthesis of the monomers.

oxidative polycondensation reaction. Also, we determined the changes of thermal, optical, and electrical characteristics related to different structures of the polymers. For this purpose, in the first part of this article, we synthesized a series of azomethine ether monomers containing —OH and/or —OCH<sub>3</sub> groups in different positions of aromatic ring. Then, we converted these monomers to poly (azomethine ether) derivatives via oxidative polycondensation reaction with using NaOCl as the oxidant. Also, to obtain higher electroconductive materials, we synthesized copper and cobalt complexes from 4,4'-oxybis[N-(2-hydroxybenzylidene)aniline] and poly-4,4'-oxybis[N-(2-hydroxybenzylidene)aniline].

In the second part, we determined the solubility properties of the synthesized monomers and polymers in different organic solvents to learn how easy these products are used in various applications. Then, we characterized the monomers, polymers, and the metal complex compounds by using UV-vis, <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, and size exclusion chromatography (SEC) techniques. Also, thermal stabilities of the products were studied by TG-DTA techniques. Optical band gaps (*E<sub>g</sub>*) were calculated from their absorption edges. Electrical properties of doped and undoped polymers and the metal complexes were determined by four-point probe technique at the room temperature and atmospheric pressure. In addition, an important increase of the conductivity was attained when iodine was employed as a doping agent.

## MATERIALS AND METHODS

### Materials

Bis(4-aminophenyl)ether, salicylaldehyde, 4-hydroxybenzaldehyde, 3,4-dihydroxy benzaldehyde, vanillin (4-hydroxy-3-methoxybenzaldehyde), Cu(AcO)<sub>2</sub> · H<sub>2</sub>O, Co(AcO)<sub>2</sub> · 4H<sub>2</sub>O, methanol, ethanol, ethyl acetate, acetonitrile, acetone, CHCl<sub>3</sub>, tetrahydrofurane, THF,

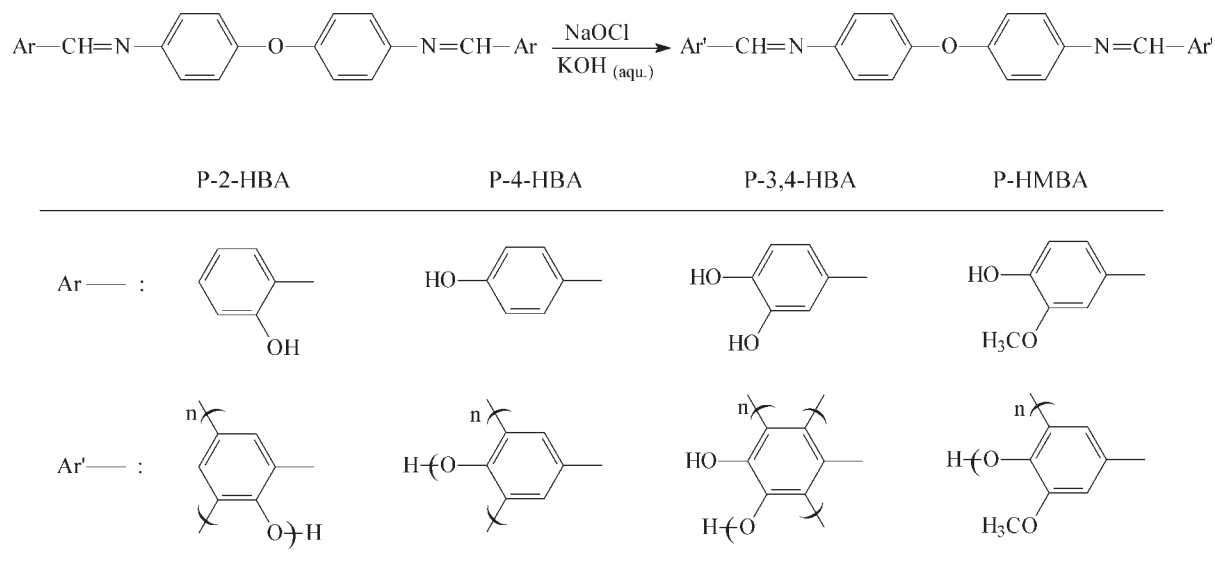
dimethylformamide, DMF, dimethylsulfoxide, DMSO, H<sub>2</sub>SO<sub>4</sub>, KOH, and HCl (37%) were supplied from Merck Chemical (Germany) and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical (Turkey).

### Synthesis of the monomers

The Schiff base monomers abbreviated as 2-HBA, 4-HBA, 3,4-HBA, and HMBA were synthesized by the condensation reaction of bis(4-aminophenyl)ether with salicylaldehyde, 4-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 4-hydroxy-3-methoxybenzaldehyde, respectively. Reactions were made as follows: Bis(4-aminophenyl)ether (0.2 g, 0.001 mol) was placed into a 250-mL three-necked round-bottom flask which was fitted with condenser, thermometer, and magnetic stirrer, and 60 mL methanol was added into the flask as a solvent. Reaction mixture was heated at boiling temperature of methanol and bis(4-aminophenyl)ether was solved. A solution of excess amount of aldehyde (0.366 g, 0.003 mol for salicylaldehyde and 4-hydroxybenzaldehyde; 0.414 g, 0.003 mol for 3,4-dihydroxybenzaldehyde, and 0.456 g, 0.003 mol for 4-hydroxy-3-methoxybenzaldehyde) in 20 mL methanol was added into the flask. Reactions were maintained for 3 h under reflux (Scheme 1). The precipitated Schiff bases were filtered, recrystallized from methanol, and dried in vacuum desiccators (yields: 94, 96, 46, and 93%, for 2-HBA, 4-HBA, 3,4-HBA, and HMBA, respectively).

### Synthesis of the polymers

The synthesized monomers were converted to their polymer derivatives through oxidative polycondensation reactions in an aqueous alkaline medium using NaOCl (30%) as the oxidant (Scheme 2), as in the literature.<sup>21</sup> Reactions were made in 250 mL three-necked round-bottom flasks which were fitted



Scheme 2 Synthesis of the polymers.

with condenser, thermometer, and magnetic stirrer. When the monomers interacted with NaOCl in alkaline medium, phenoxy radicals precipitated immediately with brown color. The oxidative polycondensation reaction conditions and the yields of polymer are shown in Table I.

#### Synthesis of the metal complex compounds of 2-HBA and P-2-HBA

A solution of  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$  (0.160 g,  $8 \times 10^{-4}$  mol) and  $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$  (0.200 g,  $8 \times 10^{-4}$  mol) in methanol (10 mL) was added to a solution of 2-HBA (0.204 g,  $5 \times 10^{-4}$  mol) and P-2-HBA (0.200 g) in tetrahydrofuran (40 mL). The mixtures were heated at  $70^\circ\text{C}$  and reactions were maintained for 5 h under reflux (Scheme 3). The precipitated monomer and polymer complexes were filtered, washed with cold methanol/THF (1 : 1), and dried in vacuum oven (yields: 94, 86, 21, and 38% for 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co complexes, respectively).

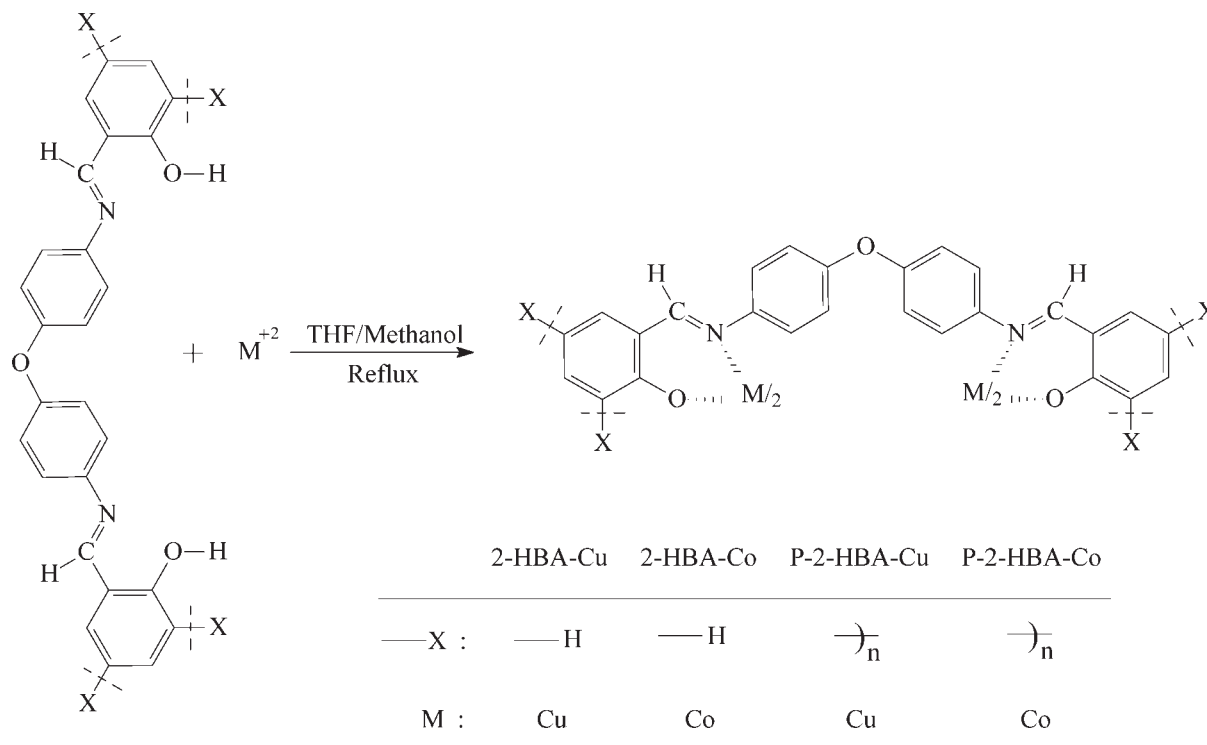
#### Characterization techniques

The infrared spectra were measured by Perkin-Elmer FTIR Spectrum one. The FTIR spectra were

recorded using universal ATR sampling accessory ( $4000\text{--}550\text{ cm}^{-1}$ ). Ultraviolet-visible (UV-vis) spectra were measured by Perkin-Elmer Lambda 25. UV-vis spectra of the synthesized compounds were determined by using methanol for the monomers and DMSO for the polymers and the complexes. The synthesized monomers and polymers were characterized by using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by deuterated DMSO- $d_6$  as a solvent at  $25^\circ\text{C}$ . Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20 and  $1000^\circ\text{C}$  (in  $\text{N}_2$ , rate  $10^\circ\text{C}/\text{min}$ ). The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) were determined by SEC techniques of Shimadzu. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d.  $\times$  300 mm columns was used; eluent: DMF/Methanol (v/v, 4/1, 0.4 mL/min), polystyrene standards. A refractive index detector was used to analyze the products at  $25^\circ\text{C}$ . Electrical conductivities were measured on a Keithley 2400 Electrometer using four-point probe technique. The pellets were pressed

TABLE I  
The Oxidative Polycondensation Reaction Conditions and the Yields of Polymers

Polymer	Temp. ( $^\circ\text{C}$ )	Reaction time (h)	[Monomer] <sub>0</sub> (mol/L)	[NaOCl] <sub>0</sub> (mol/L)	[KOH] <sub>0</sub> (mol/L)	Yield of polymer (%)
P-2-HBA	90	10	0.007	0.044	0.315	94
P-4-HBA	90	10	0.010	0.067	0.085	67
P-3,4-HBA	90	10	0.019	0.071	0.045	92
PHMBA	90	10	0.013	0.071	0.045	95



**Scheme 3** Synthesis of the metal complex compounds of monomer and polymer.

on a hydraulic press developing up to  $1687.2 \text{ kg cm}^{-2}$ . Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.<sup>20</sup> The optical band gaps ( $E_g$ ) of the synthesized compounds were calculated from their absorption edges.

## RESULTS AND DISCUSSION

### Solubility properties

All of the synthesized monomers have light colors. But the colors of their polymer derivatives are dark brown. The solubility tests were done in different

solvents by using 1 mg sample and 1 mL solvent at  $25^\circ\text{C}$  and the results are shown in Table II.

As shown in Table II the monomers are more soluble in many solvents compared with their polymers. They are all soluble in conc.  $\text{H}_2\text{SO}_4$ , DMF, and DMSO. Although the monomers are completely soluble in THF none of their polymers is soluble. Therefore, THF was used to separate unreacted monomers from the synthesized polymers after the polymerizations. Although chloroform is a good solvent for P-2-HBA and PHMBA to separate from their unreacted monomers it can not be used for P-4-HBA and P-3,4-HBA with same purpose.

**TABLE II**  
Solubility Tests of the Monomer and Polymer Compounds

Solvent	Compounds							
	2-HBA	4-HBA	3,4-HBA	HMBA	P-2-HBA	P-4-HBA	P-3,4-HBA	PHMBA
$\text{CHCl}_3$	+	—	—	+	—	—	—	—
Acetone	—	+	+	+	—	—	—	—
Ethyl acetate	—	—	±	—	—	—	—	—
Ethanol	—	—	±	—	—	—	—	—
Acetonitrile	—	—	±	—	—	—	—	—
THF	+	+	+	+	—	—	—	—
DMF	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+
$\text{H}_2\text{SO}_4$	+	+	+	+	+	+	+	+

+, soluble; —, insoluble; ±, partially soluble.

**TABLE III**  
**The Number Average Molecular Weight ( $M_n$ ), Weight Average Molecular Weight ( $M_w$ ), Polydispersity Index (PDI), and % Values of the Oxidative Polycondensation Products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA**

Compounds	Molecular weight distribution parameters														
	Total			Fraction I				Fraction II				Fraction III			
	$M_n$	$M_w$	PDI	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%	$M_n$	$M_w$	PDI	%
P-2-HBA	2,400	2,850	1.188	750	950	1.267	75	9,500	14,300	1.505	10	39,000	42,900	1.100	15
P-4-HBA	4,900	5,400	1.102	700	900	1.286	80	11,200	11,900	1.063	10	130,000	144,000	1.108	10
PHMBA	23,400	25,700	1.098	650	900	1.385	30	11,600	13,000	1.121	35	189,000	206,600	1.093	35
P-3,4-HBA	31,200	41,700	1.337	600	850	1.417	10	11,000	11,400	1.036	25	139,800	188,400	1.348	65

However, with exception of 2-HBA the synthesized monomers are soluble in acetone whereas their polymers are not (see Table II). These all mean that the synthesized poly(azomethine ethers) have higher resistant to solubility in many organic solvents with comparison to their monomers.

#### Structures of the synthesized compounds

According to the SEC chromatograms, the values of number-average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and PDI of P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA were calculated according to a Polystyrene standard calibration curve and given in Table III. According to the SEC analysis, the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and PDI values were found to be 2400, 2850 g mol<sup>-1</sup> and 1.188 for P-2-HBA, 4900, 5400 g mol<sup>-1</sup> and 1.102 for P-4-HBA, 23,400, 25,700 g mol<sup>-1</sup> and 1.098 for PHMBA, and 31,200, 41,700 g mol<sup>-1</sup> and 1.337 for P-3,4-HBA, respectively. According to these results, P-3,4-HBA and PHMBA have quite high molecular weights and lower PDI values when compared to the previously presented oligophenol derivatives,<sup>15-19</sup> while the others' are similar with literature values. HMBA contains -OCH<sub>3</sub> substituent in the structure, and this substituent likely makes this monomer more soluble. So, during the growing up of the polymer chains, PHMBA keeps the solubility for a long time and consequently longer polymer molecules are obtained. Also, 3,4-HBA has two -OH groups where the radicalic polymerization begins. This supplies the molecule radicalic stability during the oxidative polycondensation and so high molecular weight depending on the high ratio of the intermolecular combinations of 3,4-HBA units.

The FTIR spectra of the oxidative polycondensation products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA are different by broadening and shifting of the peaks from the FTIR spectra of the monomers. Also the numbers of the peaks of the polymers are less than the monomers. To identify the structures of the monomers and the polymers, <sup>1</sup>H NMR and <sup>13</sup>C

NMR spectra were recorded in DMSO-*d*<sub>6</sub>. To identify the metal complex compounds, the UV-vis and FTIR spectra were recorded. At the FTIR spectra of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co the new peaks indicating metal-N and metal-O coordinations were observed between 550 and 700 cm<sup>-1</sup>. The results of UV-vis, FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR analyses were shown in Table IV.

Coupling selectivity of oligophenol derivatives have been previously studied and reported in the literatures.<sup>22</sup> Crosslinking in polymer structures is expected in those cases where the ortho and para positions (C-C coupling) and oxyphenylene (C-O-C coupling) in the corresponding monomer structures if they are unsubstituted. At the <sup>1</sup>H NMR spectra of the polymers, the integration areas of -OH protons were used to determine the rate of the C-O-C coupling to C-C coupling. According to these values the polymerization of the 2-HBA and 4-HBA largely maintained with C-O-C coupling whereas at the polymerization of the 3,4-HBA and HMBA C-O-C coupling is less than C-C coupling. Additionally, it is seen in the <sup>13</sup>C NMR spectra of the polymers, the integration areas of -OH protons were used to determine the rate of the C-O-C coupling to C-C coupling. According to these values the polymerization of the 2-HBA and 4-HBA largely maintained with C-O-C coupling whereas at the polymerization of the 3,4-HBA and HMBA C-O-C coupling is less than C-C coupling. Additionally, it is seen in the <sup>13</sup>C NMR spectra of P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA that the C-C coupling between any two adjacent phenyl rings are largely at ortho and para positions of the -OH groups. However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The peak values for C3 and C5 were observed in 123.60 and 117.93 ppm for 2-HBA and 133.45 (showing as C14) and 123.23 ppm (new peaks) for P-2-HBA, respectively. The peaks observed at 115.98 and 114.58 ppm at the <sup>13</sup>C NMR spectra of 3,4-HBA for C2 and C5 shifted at 122.67 and 121.13 ppm at the <sup>13</sup>C NMR spectra of P-3,4-HBA, respectively. Also, the peak at 115.82 ppm of the <sup>13</sup>C NMR spectra of HMBA for C2 shifted at 124.78 ppm at the spectra of PHMBA. These changes indicate that the polymerization progress includes the C-C coupling system. The reaction mechanism on the coupling selectivity has been studied by Ayyagari coworkers and Kaya and coworkers and three possible reaction mechanisms for the C-C



**TABLE IV**  
**UV-vis, FTIR, and NMR Spectral Characterization Results of the Synthesized Compounds**

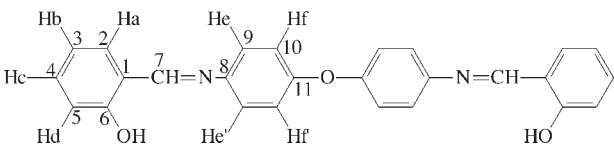
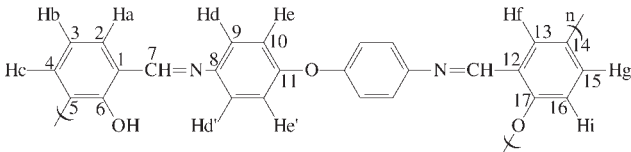
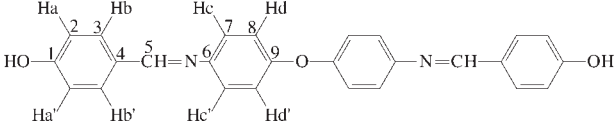
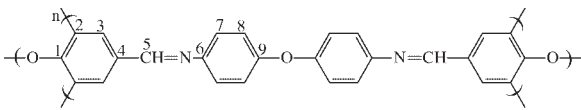
Compound	Spectral data
2-HBA	<p>UV-vis: <math>\lambda</math>/nm: 273, 352</p> <p>IR: <math>\nu/\text{cm}^{-1}</math>: 3210 (OH), 3054 (C-H, Phenyl), 1614 (C=N), 1569, 1489, 1456 (C=C phenyl), 1260 (C-O-C), 1281 (C-OH)</p> <p><math>^1\text{H-NMR}</math> (DMSO): <math>\delta</math> ppm: 13.05 (s, 2H, -OH), 8.97 (s, 2H, -CH=N-), 7.65 (d, 2H, -Ha), 7.51 (d, 4H, -He, -He'), 7.42 (t, 2H, -Hc), 7.15 (d, 4H, -Hf, -Hf'), 6.97 (m, 4H, -Hb, -Hd)</p> <p><math>^{13}\text{C-NMR}</math> (DMSO): ppm: 163.23 (C7-H), 160.66 (C6-ipso), 155.04 (C11-ipso), 143.05 (C8-ipso), 133.65 (C4-H), 132.96 (C2-H), 123.60 (C3-H), 120.01 (C9-H), 119.64 (C1-ipso), 117.93 (C5-H), 117.05 (C10-H)</p> 
P-2-HBA	<p>UV-vis: <math>\lambda</math>/nm: 262, 323, 346, 470</p> <p>IR: <math>\nu/\text{cm}^{-1}</math>: 3350 (OH), 3044 (C-H, Phenyl), 1618 (C=N), 1569, 1488 (C=C phenyl), 1263, 1227 (C-O-C), 1282 (C-OH)</p> <p><math>^1\text{H-NMR}</math> (DMSO): <math>\delta</math> ppm: 13.15 (s, -OH), 8.98 (s, 2H, -CH=N-), 7.65 (s, 1H, -Hf), 7.51 (d, 1H, -Ha), 7.41 (d, 4H, -Hd), 7.15 (d, 4H, -He), 6.98 (d, 1H, -Hg), 6.79 (d, 1H, -Hc), 6.62 (t, 1H, -Hb), 6.51 (d, 1H, -Hi)</p> <p><math>^{13}\text{C-NMR}</math> (DMSO): ppm: 163.15 (C7-H), 162.32 (C6-ipso), 160.60 (C11-ipso), 158.48 (C17-ipso), 148.91 (C8-ipso), 145.91 (C15-H), 142.30 (C4-H), 133.45 (C14-ipso), 132.85 (C2, C13-H), 123.23 (C5-ipso), 121.41 (C3-H), 119.50 (C9-H), 117.62 (C1-ipso), 116.99 (C12-ipso), 115.39 (C10, C16-H)</p> 
4-HBA	<p>UV-vis: <math>\lambda</math>/nm: 252, 289, 336</p> <p>IR: <math>\nu/\text{cm}^{-1}</math>: 3426 (OH), 3061 (C-H, Phenyl), 1623 (C=N), 1588, 1512, 1496 (C=C phenyl), 1245 (C-O-C), 1281 (C-OH)</p> <p><math>^1\text{H-NMR}</math> (DMSO): <math>\delta</math> ppm: 10.15 (s, 2H, -OH), 8.48 (s, 2H, -CH=N-), 7.78 (d, 4H, -Hb, -Hb'), 7.27 (d, 4H, -Hc, -Hc'), 7.04 (d, 4H, -Hd, -Hd'), 6.90 (d, 4H, -Ha, -Ha')</p> <p><math>^{13}\text{C-NMR}</math> (DMSO): ppm: 161.02 (C5-H), 159.76 (C1-ipso), 155.19 (C9-ipso), 147.81 (C6-ipso), 131.06 (C3-H), 128.04 (C4-ipso), 122.75 (C7-H), 119.65 (C8-H), 116.13 (C2-H)</p> 
P-4-HBA	<p>UV-vis: <math>\lambda</math>/nm: 286, 332</p> <p>IR: <math>\nu/\text{cm}^{-1}</math>: 3345 (OH), 3036 (C-H, Phenyl), 1621 (C=N), 1582, 1491 (C=C phenyl), 1226 (C-O-C), 1280 (C-OH)</p> <p><math>^1\text{H-NMR}</math> (DMSO): <math>\delta</math> ppm: 9.79 (s, -OH), 8.48 (s, 2H, -CH=N-), 5.65-7.30 (m, aromatic)</p> <p><math>^{13}\text{C-NMR}</math> (DMSO): ppm: 160.3 (C5-H), 159.0 (C1-ipso), 154.5 (C9-ipso), 144.0 (C6-ipso), 130.1 (C3-H), 124.6 (C4-ipso), 121.8 (C2-ipso), 117.1 (C7-H), 115.3 (C8-H)</p> 
3,4-HBA	<p>UV-vis: <math>\lambda</math>/nm: 256, 288, 344, 435</p> <p>IR: <math>\nu/\text{cm}^{-1}</math>: 3288 (OH), 3034 (C-H, Phenyl), 1597 (C=N), 1586, 1518, 1493 (C=C phenyl), 1241 (C-O-C), 1279 (C-OH)</p> <p><math>^1\text{H-NMR}</math> (DMSO): <math>\delta</math> ppm: 9.53 (s, 4H, -OH), 8.41 (s, 2H, -CH=N-), 7.45 (d, 2H, -Hb), 7.27 (d, 4H, -Hd, -Hd'), 7.21 (s, 2H, -Hc), 7.05 (d, 4H, -He, He'), 6.88 (d, 2H, -Ha)</p> <p><math>^{13}\text{C-NMR}</math> (DMSO): ppm: 159.96 (C7-H), 155.16 (C11-ipso), 149.64 (C1-ipso), 147.77 (C6-ipso), 146.14 (C8-ipso), 128.55 (C4-ipso), 125.08 (C3-H), 122.92 (C9-H), 119.66 (C10-H), 115.98 (C2-H), 114.58 (C5-H)</p>

TABLE IV Continued

Compound	Spectral data
P-3,4-HBA	UV-vis: $\lambda$ /nm: 259, 341, 444 IR: $\nu$ /cm <sup>-1</sup> : 3378 (OH), 3071 (C—H, Phenyl), 1587 (C=N), 1492, 1449 (C=C phenyl), 1229, 1212 (C—O—C), 1289 (C—OH) <sup>1</sup> H-NMR (DMSO): $\delta$ ppm: 9.29 (s, —OH), 8.41 (s, 2H, —CH=N—), 7.39 (d, 2H, -Hb), 7.20 (d, 4H, -Hd, -Hd'), 7.06 (s, -Hc-terminal), 6.88 (d, 4H, -He, -He'), 6.69 (d, -Ha-terminal) <sup>13</sup> C-NMR (DMSO): ppm: 159.32 (C7-H), 157.20 (C11-ipso), 152.61 (C1-ipso), 149.66 (C6-ipso), 146.09 (C8-ipso), 129.32 (C4-ipso), 124.97 (C3-H), 122.67 (C2-ipso), 121.13 (C5-ipso), 119.45 (C9-H), 117.70 (C10-H)
HMBA	UV-vis: $\lambda$ /nm: 232, 285, 339, 437 IR: $\nu$ /cm <sup>-1</sup> : 3509 (OH), 3036 (C—H, Phenyl), 2984 (C—H, aliphatic), 1621 (C=N), 1601, 1509, 1493 (C=C phenyl), 1234 (C—O—C), 1273 (C—OH) <sup>1</sup> H-NMR (DMSO): $\delta$ ppm: 9.78 (s, 2H, —OH), 8.48 (s, 2H, —CH=N—), 7.54 (s, 2H, -Hc), 7.34 (d, 2H, -Hb), 7.28 (d, 4H, -Hd, -Hd'), 7.05 (d, 4H, -He, -He'), 6.91 (d, 2H, -Ha), 3.87 (s, 6H, —OCH <sub>3</sub> ) <sup>13</sup> C-NMR (DMSO): ppm: 159.98 (C8-H), 155.19 (C12-ipso), 150.49 (C1-ipso), 148.54 (C6-ipso), 147.76 (C9-ipso), 128.46 (C4-ipso), 124.47 (C3-H), 122.80 (C10-H), 119.67 (C11-H), 115.82 (C2-H), 110.70 (C5-H), 55.97 (C7-ipso)
PHMBA	UV-vis: $\lambda$ /nm: 258, 270, 362 IR: $\nu$ /cm <sup>-1</sup> : 3222 (OH), 3070 (C—H, Phenyl), 2932 (C—H, aliphatic), 1578 (C=N), 1563, 1495 (C=C phenyl), 1223 (C—O—C), 1280 (C—OH) <sup>1</sup> H-NMR (DMSO): $\delta$ ppm: 9.29 (s, —OH), 7.83 (s, 2H, —CH=N—), 7.31 (s, 2H, -Hc), 7.01 (s, 2H, -Hb), 6.93 (d, 4H, -Hd, -Hd'), 6.84 (d, 4H, -He, -He'), 6.69 (d, -Ha-terminal), 3.74 (s, 6H, —OCH <sub>3</sub> ) <sup>13</sup> C-NMR (DMSO): ppm: 158.51 (C8-H), 156.85 (C12-ipso), 155.10 (C1-ipso), 147.31 (C6-ipso), 145.48 (C9-ipso), 126.00 (C4-ipso), 124.78 (C2-ipso), 122.84 (C3-H), 121.24 (C10-H), 117.73 (C11-H), 116.20 (C5-H), 56.51 (C7-ipso)
2-HBA-Cu	UV-vis: $\lambda$ /nm: 228, 295, 392 IR: $\nu$ /cm <sup>-1</sup> : 3349 (OH), 3056 (C—H, Phenyl), 1606 (C=N), 1587, 1532, 1492 (C=C, phenyl), 1236 (C—O—C), 1296 (C—OH), 594 (Cu—O), 689 (Cu—N)
2-HBA-Co	UV-vis: $\lambda$ /nm: 299, 378 IR: $\nu$ /cm <sup>-1</sup> : 3337 (OH), 3053 (C—H, Phenyl), 1615 (C=N), 1568, 1502, 1490 (C=C, phenyl), 1238 (C—O—C), 1282 (C—OH), 587 (Cu—O), 652 (Cu—N)
P-2-HBA-Cu	UV-vis: $\lambda$ /nm: 299, 402 IR: $\nu$ /cm <sup>-1</sup> : 3403 (OH), 3056 (C—H, Phenyl), 1606 (C=N), 1587, 1532, 1492 (C=C phenyl), 1236 (C—O—C), 1298 (C—OH), 594 (Co—O), 616 (Co—N)
P-2-HBA-Co	UV-vis: $\lambda$ /nm: 258, 298, 387 IR: $\nu$ /cm <sup>-1</sup> : 3346 (OH), 3010 (C—H, Phenyl), 1607 (C=N), 1575, 1533, 1492 (C=C phenyl), 1238 (C—O—C), 1290 (C—OH), 595 (Co—O), 664 (Co—N)

TABLE V  
Thermal Degradation Values of the Synthesized Monomer, Polymer, and  
Monomer/Polymer-Metal Complex Compounds

Compounds	$T_{on}^a$	$T_{max}^b$	20% weight losses	50% weight losses	% Carbine residue at 1000°C	DTA	
						Exo	Endo
2-HBA	333	369	340	364	14.71	–	209
P-2-HBA	177, 420	260, 497	423	847	39.23	–	–
2-HBA-Cu	159, 310	219, 341, 494	264	888	46.48	–	–
2-HBA-Co	154, 379	171, 409	382	895	44.69	–	174
P-2-HBA-Cu	159, 313	198, 348, 511	336	548	40.03	–	–
P-2-HBA-Co	307	340, 506	486	653	29.71	–	–
4-HBA	251	269, 434	441	–	60.43	–	247
P-4-HBA	140, 310	172, 342, 530	433	925	43.92	–	–
3,4-HBA	218	232, 302, 447	382	–	53.70	228	218
P-3,4-HBA	257	354, 453	417	954	49.00	–	–
HMBA	269	301	315	–	51.30	–	162
PHMBA	145	184, 486	424	981	49.72	–	–

<sup>a</sup> The onset temperature.

<sup>b</sup> Maximum weight temperature.

and oxyphenylene C—O—C coupling systems have been proposed in the literature.<sup>23–25</sup>

### Thermal analysis

According to TGA, DTG, and DTA curves the calculated thermal degradation data were given in Table V. As seen in the Table V, the initial degradation temperature (°C) and the carbine residue (%) at 1000°C are 333 and 14.71 for 2-HBA, 177, 420, and 39.23 for P-2-HBA, 159, 310, and 46.48 for 2-HBA-Cu, 154, 379, and 44.69 for 2-HBA-Co, 159, 313, and 40.03 for P-2-HBA-Cu, and 307 and 29.71 for P-2-HBA-Co, respectively. According to these values P-2-HBA is more stable than 2-HBA through to temperature and thermal decomposition. Because of long conjugated bond systems, the polymer demonstrated higher resistance against high temperature than the monomer. In addition, the metal complexes have higher carbine residue at 1000°C than the monomer and polymer (except for P-2-HBA-Co). According to thermal analysis results, copper complexes were demonstrated higher thermal stability than the cobalt complexes and these results agree with the previous studies in which Schiff base derivatives of oligosalicylaldehyde were used.<sup>18,19</sup>

Thermal degradation data of 4-HBA, 3,4-HBA, HMBA, and their polymers were also given in Table V. Looking at these values, the initial degradation temperature (°C) and the carbine residue (%) at 1000°C are 251 and 60.43 for 4-HBA, 140, 310, and 43.92 for P-4-HBA, 218 and 53.70 for 3,4-HBA, 257 and 49.00 for P-3,4-HBA, 269 and 51.30 for HMBA, and 145 and 49.72 for PHMBA, respectively. According to these values, the oxidative polycondensation products of 4-HBA, 3,4-HBA, and HMBA are less stable than their monomers through to temperature

and thermal decomposition. Although the initial degradation temperature of P-3,4-HBA is higher than 3,4-HBA, its total weight losses at 1000°C is higher. Additionally, although the weight losses of 3,4-HBA and HMBA at 1000°C are close near their polymers, the difference between the weight losses of 4-HBA and P-4-HBA is high.

As seen in the thermal decomposition ratios of the synthesized polymers at 1000°C P-2-HBA and P-4-HBA have lower thermal stabilities than P-3,4-HBA and PHMBA. This is owing to the more C—O—C coupling of P-2-HBA and P-4-HBA, as mentioned earlier. This etheric bond makes the structure unstable. Also, due to this weak bond, P-4-HBA has lower thermal stability than its monomer.

According to thermal degradation values, the synthesized polymers and their copper and cobalt complexes are also more stable than the previously presented oligophenol derivatives and metal complex compounds.<sup>16–19</sup>

### Electrical conductivities

Electrical conductivities of the synthesized polymers and the metal complexes and the changes of these values related to doping time with iodine were determined and shown in Table VI. The changes of the electrical conductivities are also given schematically in Figure 1(a) (for polymers) and Figure 1(b) (for the metal complexes). As seen in Table VI, the initial conductivities of the synthesized polymers and the metal complex compounds are quite near at about  $10^{-11}$ – $10^{-10}$  S cm<sup>-1</sup>. When doped with iodine for 168 h, the conductivities of P-2-HBA, P-4-HBA, and P-3,4-HBA could be increased by about three orders of magnitude (up to  $10^{-7}$  S cm<sup>-1</sup>, see Fig. 1). But the conductivity of PHMBA could be increased

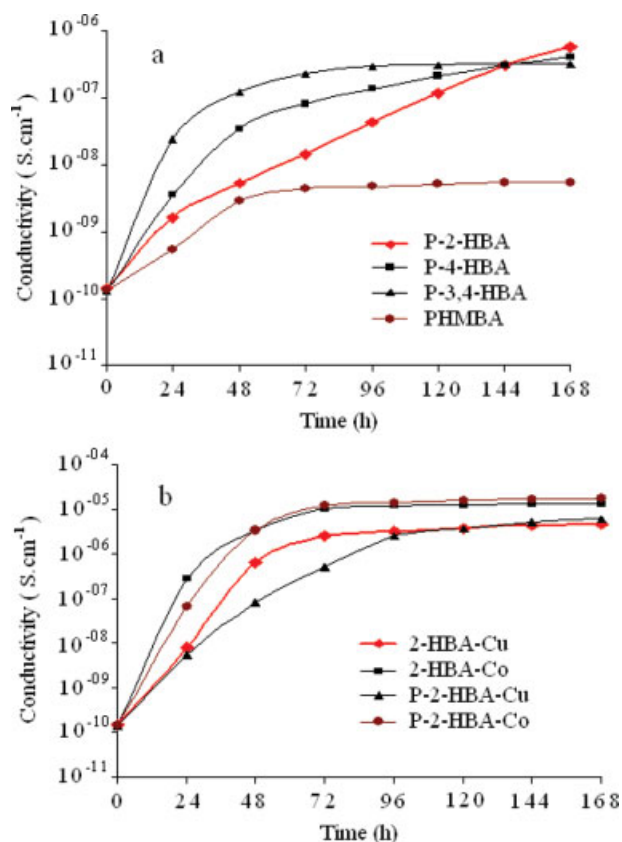


**TABLE VI**  
**Electrical Conductivity of I<sub>2</sub>-Doped Synthesized Monomer, Polymer, and Monomer/Polymer-Metal Complex Compounds vs. Doping Time at 25°C**

Doping time (h)	Conductivity (S cm <sup>-1</sup> ) × 10 <sup>-10</sup>							
	P-2-HBA	P-4-HBA	P-3,4-HBA	PHMBA	2-HBA-Cu	2-HBA-Co	P-2-HBA-Cu	P-2-HBA-Co
0	1.4142	1.2584	1.2643	1.3207	1.5056	1.3999	1.4517	1.4710
24	16.109	35.138	236.46	5.3728	81.179	2778.2	54.753	650.17
48	53.091	345.90	1211.6	28.718	6323.7	33361	854.96	3360.1
72	141.96	806.15	2278.3	44.926	26108	105018	5118.9	119018
96	435.48	1351.6	2910.2	47.201	33002	124043	26425	142261
120	1197.3	2090.9	3058.1	51.744	38694	130673	38911	163934
144	3114.3	3126.9	3141.4	54.318	44097	133021	52083	172005
168	5788.2	4159.8	3198.2	55.520	48782	134941	61225	182301

only up to about 10<sup>-9</sup> S cm<sup>-1</sup>. This is due to the steric barrier of -OCH<sub>3</sub> group, to prevent the complexation of iodine ions with imine nitrogen and so doping procedure does not occur adequately. The conductivities of the metal complex compounds also increased by about five orders of magnitude [up to 10<sup>-5</sup> S cm<sup>-1</sup>, see Fig. 1(b)] with doping time. According to these results, the synthesized polymers have higher initial and maximal conductivities than

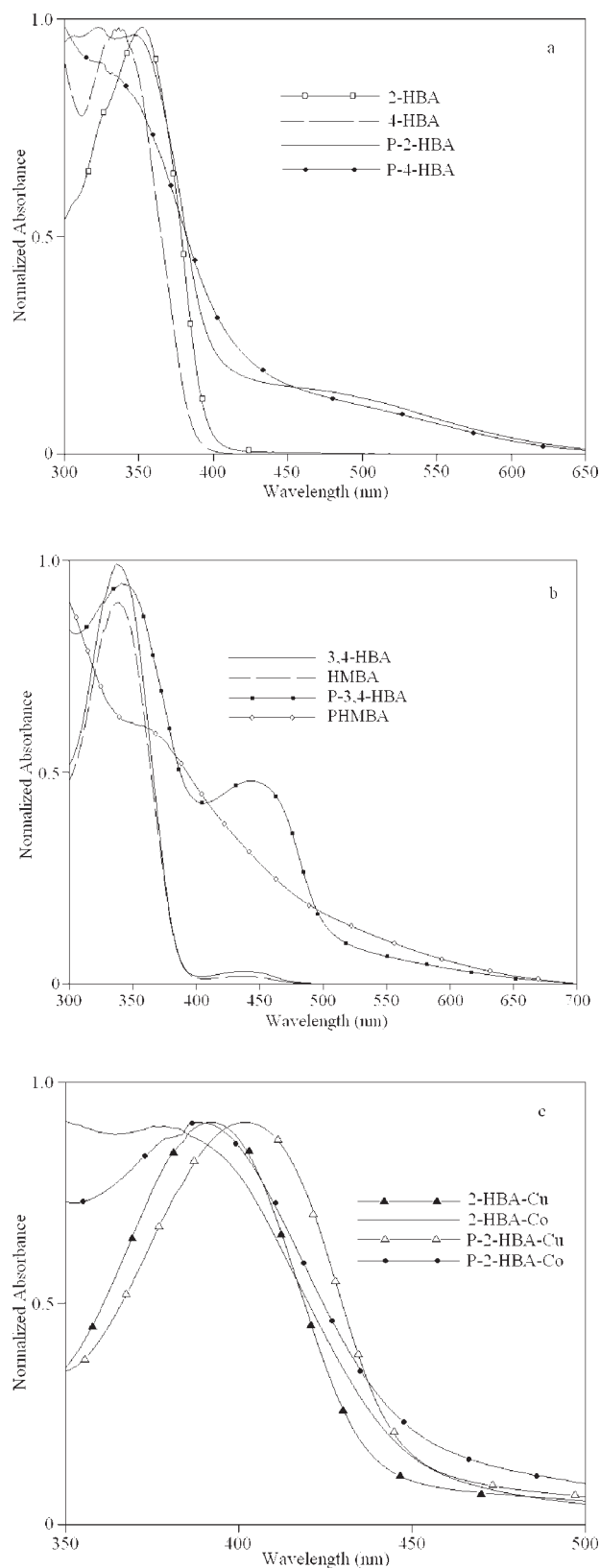
the previous studies.<sup>26</sup> In the doping of the polymers and the metal complexes with iodine, it was found that the conductivities firstly increase greatly with doping time, but then tend to level-off. For P-2-HBA only the changes of the conductivity is nearly linear [see Fig. 1(a)]. The increasing conductivity could indicate that a charge-transfer complex between the polymers (or metal complexes) and dopant iodine is continuously formed. Consequently, Figure 1 not only shows the conductivity and doping time relationship but also indicate how quickly the doping reaction takes place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curves vary with doping conditions. To exclude the influence of doping conditions, the conductivities of the doped polymers and complexes have been related with doping extent (shown in Fig. 1). Nitrogen is a very electronegative element and it is capable of coordinating with iodine ions. On the nitrogen atom, coordination of iodine ions with Schiff base polymers and pyridine solutions had been suggested in the literatures.<sup>27-30</sup>



**Figure 1** Electrical conductivity of I<sub>2</sub>-doped a = [P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA] and b = [2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co] versus doping time at 25°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Optical properties

The absorption spectra of 2-HBA, 4-HBA, P-2-HBA, and P-4-HBA recorded by using methanol and DMSO for the monomers and polymers, respectively, were shown in Figure 2(a).  $\lambda_{\max}$  and the optical band gaps values were calculated as in the literature<sup>31</sup> and shown in Table VII. As seen in Table VII,  $\lambda_{\max}$  (nm) and the optical band gaps ( $E_g$ , eV) are 352 and 3.15 for 2-HBA, 470 and 2.06 for P-2-HBA, 336 and 3.23 for 4-HBA, and 332 and 3.02 for P-4-HBA, respectively. The absorption spectra of 3,4-HBA, P-3,4-HBA, HMBA, and PHMBA were also recorded and shown in Figure 2(b). The calculated  $\lambda_{\max}$  and the optical band gaps were given in Table VII. According to these values,  $\lambda_{\max}$  (nm) and the optical band gaps values ( $E_g$ /eV) of 3,4-HBA, P-3,4-HBA, HMBA, and PHMBA are 435 and 2.61, 44, and



**Figure 2** Absorption spectra of a = [2-HBA, 4-HBA, P-2-HBA, and P-4-HBA], b = [3,4-HBA, HMBA, P-3,4-HBA, and PHMBA], and c = [2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co].

**TABLE VII**  
 $\lambda_{\max}$  and Optical Band Gap ( $E_g$ ) Values of Synthesized Compounds Calculated from Absorption Spectra

Compounds	$\lambda_{\max}$ (nm)	$E_g$ (eV)
2-HBA	352	3.15
P-2-HBA	470	2.06
2-HBA-Cu	392	2.83
2-HBA-Co	378	2.77
P-2-HBA-Cu	402	2.78
P-2-HBA-Co	387	2.78
4-HBA	336	3.23
P-4-HBA	332	3.02
3,4-HBA	435	2.61
P-3,4-HBA	444	2.47
HMBA	437	2.64
PHMBA	362	2.42

2.47, 437, and 2.64 and 362 and 2.42, respectively. The oxidative polycondensation products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA have lower band gaps than their monomers due to their polyconjugated structures. The absorption spectra of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co were recorded by using DMSO and shown in Figure 2(c). The calculated  $\lambda_{\max}$  and the optical band gaps from Figure 2(c) were also given in Table VII. According to these values,  $\lambda_{\max}$  (nm) and the optical band gaps values ( $E_g$ /eV) of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co are 392 and 2.83, 378 and 2.77, 402 and 2.78, and 387 and 2.78, respectively.

## CONCLUSIONS

Novel Schiff base monomers abbreviated as 2-HBA, 4-HBA, 3,4-HBA, and HMBA were synthesized and converted to their polycondensation products shown as P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA, respectively, via oxidative polycondensation reaction. The integration areas of the —OH protons in the  $^1\text{H}$  NMR spectra demonstrated that the 2-HBA and 4-HBA mainly polymerized with C—O—C coupling, whereas 3,4-HBA and HMBA mainly polymerized with C—C coupling. This suggestion is also the reason of thermal stability values of the polymers. Highly C—C coupling makes P-3,4-HBA and PHMBA more thermally stable than the others. These polymers were found to have carbene residue of 49–50% at 1000°C. Solubility tests showed that the synthesized polymers are completely soluble in DMF, DMSO, and  $\text{H}_2\text{SO}_4$ . Also, according to SEC analysis, P-3,4-HBA and PHMBA have quite higher molecular weights than the others. Electrical conductivities of the synthesized polymers versus doping time with iodine ions were also measured, and these results showed that the synthesized polymers have higher initial and maximal conductivities than the previous oligophenol derivatives (except PHMBA,

because of barrier effect of methoxy groups). 2-HBA and P-2-HBA metal complexes shown as 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co were also synthesized and with doping with iodine their conductivities were found to reach up to  $10^{-5}$  S  $\text{cm}^{-1}$  in cobalt complexes and up to  $10^{-6}$  S  $\text{cm}^{-1}$  in copper complexes. Consequently, the electrical conductivity measurements showed that the synthesized polymers and the metal complexes are semiconductors and their conductivities would be increased considerably via doping with iodine. The optical band gap values of the polymers were found to be higher than their monomers. This is because of the polyconjugated structures of the polymers. The observed band gaps are sufficiently low to make these polymers and metal complexes highly promising for electronic and optoelectronic applications.

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